

# MEMORANDUM



# MWH

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**Reference:** P4 Production Southeast Idaho Mine-Specific Selenium Program

**Subject:** Laboratory Split Data for May 2004 Forage Fish and Salmonid Sampling – Draft

## Introduction

This memorandum documents the results and preliminary interpretation of the laboratory split fish tissue data (forage fish and salmonid). All samples were collected and analyzed as specified in the *Comprehensive Site Investigation, Sampling and Analysis Plan—Final* (MWH, 2004). Both whole-body and fillet tissue samples were analyzed for the designated contaminants of potential concern (COPC), which include total selenium (Se), total cadmium (Cd), total nickel (Ni), total vanadium (V), and total zinc (Zn).

Approximately 10% of the sampled stations were designated as quality assurance/quality control (QA/QC) stations for replicate analysis. Tissue samples were sent to the primary analysis laboratory, ACZ. ACZ received, processed, and submitted split solid matrix samples to the University of Idaho (UI) for QA/QC analyses.

## Sample Preparation and Analysis

Two types of fish samples were collected: forage fish (whole-body) and salmonid fish (fillet-with-skin and whole-body) at each station. Only whole-body forage fish and salmonid split samples were submitted to UI for QA/QC analysis. Fish samples for split analysis were designated in the field.

Whole body samples were weighed and homogenized by ACZ. Two splits of the homogenized tissue sample were aliquoted prior to being refrozen. One split was retained by ACZ and the other was shipped to UI under ACZ chain of custody in a 4°C cooler with ice.

Frozen sub-samples were analyzed by both laboratories on a wet weight basis. UI required a minimum of 20 grams of wet sample for analysis, and therefore was unable to additionally analyze the samples for moisture content in addition to the COPC analytes. ACZ analyzed the samples for both moisture content and the COPC analytes. The ACZ moisture content result for each respective sample was used to dry-weight correct the UI results.

## **Results and Discussion**

Analytical results for split-samples analyzed by both ACZ and UI are shown in Table 1 for forage fish (whole-body) and Table 2 for salmonids (whole-body). The relative difference (RD) between the two results has been calculated, and the 95% two-sided confidence bound has been calculated for the average RD for each matrix and analyte. If the bounds do not encompass zero, the result has been shaded.

The evaluation of field replicates is included in the EPA Functional Guidelines for Inorganic Data Review (USEPA, 2004), however no qualification criteria has been established. No guidance has been established by the EPA for the evaluation of laboratory splits. The laboratory and EPA established criterion for solid sample results (that are  $> 5x$  the associated reporting limit) is an RD of  $< 0.35$ . For the purposes of this study the criterion for the evaluation of laboratory replicates has been arbitrarily set as twice the laboratory duplicate criterion. Therefore the project-specific RD criterion has been set at  $< 0.70$ .

The overall assessment shows a general positive bias in the UI data when compared to the ACZ data. This is likely due to moisture loss resulting from the freeze-thaw cycles following the homogenization performed by ACZ. For all future analyses, the moisture content of the sub-samples should be determined at the time of sample analyses to minimize any bias caused by moisture loss.

### ***Forage Fish***

For the analysis of Se in forage fish, the mean 95% confidence bound does not encompass zero, indicating that there is a difference between the two reported results for this analyte. However inspection of the RD for each sample station shows that the precision between the two laboratories meets the project specific RD criterion of 0.70.

For the analysis of Cd, Ni, V, and Zn, the mean 95% confidence bound does encompass zero, indicating that there is no significant difference between the two reported results for these analytes.

### ***Salmonids***

For the analysis of Se in salmonids, the mean 95% confidence bound does not encompass zero, indicating that there is a difference between the two reported results for this analyte. However inspection of the RD for each sample station shows that the precision between the two laboratories meets the project-specific RD criterion of 0.70.

For the analysis of Cd, Ni, and Zn, the mean 95% confidence bound does encompass zero, indicating that there is no significant difference between the two reported results for these analytes.

For the analysis of V, the mean 95% confidence bound does not encompass zero, indicating that there is a difference between the two reported results for this analyte. Inspection of the RD shows that the precision between the two laboratories does not meet the project specific RD criterion of 0.70, and there is a significant bias for this analyte that should be investigated.

## **Conclusions**

Comparison of the two data sets (forage fish and salmonids) shows agreement between the two independent laboratories and may assist in identifying potential systematic biases associated with sampling and analysis. Overall comparison of laboratory split data demonstrates the utility of moisture content analysis by each laboratory to remove any bias caused by moisture loss during shipment. However, the positive bias of the UI data when compared to the ACZ is not significant for the majority of the COPC analytes in this study.

## **References**

US Environmental Protection Agency, 2004. "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" Publication 9240.1-45, EPA/540/R/04/004. Office of Superfund Remediation and Technology Innovation, USEPA, Washington, D. C.

MWH, 2004. "Comprehensive Site Investigation, Sampling and Analysis Plan—Final", P4 Production Southeast Idaho Mine-Specific Selenium Program. March. Seattle, WA.

<b>Table 1</b> <b>May 2004 Forage Fish QA Station Data Comparison (mg/kg dw) - Censored Data (1/2 RL)</b>											
	Station ID	Selenium	Flag	Cadmium	Flag	Nickel	Flag	Vanadium	Flag	Zinc	Flag
Blackfoot River, Below Ballard Creek	MST019-QA1-R1 <sup>a</sup>	7.0		0.12		1.8		1.1		76	
	MST019-QA2 <sup>b</sup>	8.0	J	0.080	U	1.3	J	1.5	U	76	
	RD	-0.13		0.41		0.33		-0.31		0.0	
Blackfoot River, Below Wooley Valley Creek	MST022-QA1-R2 <sup>a</sup>	7.4		0.060	U	1.6		0.98		61	
	MST022-QA2 <sup>b</sup>	10	J	0.085	U	1.3	J	1.7	U	83	
	RD	-0.30		-0.35		0.21		-0.56		-0.31	
Blackfoot River, Above Wooley Range Ridge Creek	MST026-QA1-R1 <sup>a</sup>	2.2		0.065	U	4.4		0.36		87	
	MST026-QA2 <sup>b</sup>	3.2	J	0.085	U	1.1	J	1.7	U	78	
	RD	-0.38		-0.27		1.5		-1.7		0.11	
Meadow Creek, Above Blackfoot Reservoir	MST235-QA1-R2 <sup>a</sup>	1.4		0.11		8.9		0.97		78	
	MST235-QA2 <sup>b</sup>	2.0	J	0.080	U	1.0	J	1.5	U	96	
	RD	-0.36		0.32		2.6		-0.44		-0.21	
<i>mean of RD</i>		-0.29		0.027		1.2		-0.76		-0.10	
<i>standard deviation of RD</i>		0.11		0.39		1.1		0.65		0.19	
<i>sample size</i>		4		4		4		4		4	
<i>mean<sub>0.025</sub></i>		-0.47		-0.60		-0.65		-1.8		-0.41	
<i>mean<sub>0.975</sub></i>		-0.12		0.65		3.0		0.27		0.20	
<b>NOTES:</b> <sup>a</sup> ACZ QA station result. <sup>b</sup> U of I QA station result. <sup>c</sup> Percent dissolved solids were not reported for UI results, therefore the ACZ QA station results was used. (RD) - Relative Difference between the UI lab result and the ACZ lab results. For each sample station, the RD has been calculated. If the RD > 0.70, the result has been shaded. For each analyte, the 95% two-sided confidence bound has been calculated. If the bounds do not encompass zero, the result has been shaded. <b>Data qualifier definitions are:</b> (U) - The material was analyzed for, but was not detected above the level of the associated value. These values have been censored and are equal to one-half the reporting limit. (J) - The associated value is an estimated quantity.											

<b>Table 2</b> <b>May 2004 Salmonid QA Station Data Comparison (mg/kg dw) - Censored Data (1/2 RL)</b>											
	Station ID	Selenium	Flag	Cadmium	Flag	Nickel	Flag	Vanadium	Flag	Zinc	Flag
Blackfoot River, Below Dry Valley Creek	MST023-QA2 <sup>a</sup>	9.1		0.046	U	0.77		1.0		120	
	MST023-QA3 <sup>b</sup>	10	J	0.095	U	2.1	J	1.8	U	150	
	RD	-0.094		-0.74		-1.0		-0.60		-0.22	
Blackfoot River, Below Angus Creek	MST027-QA2 <sup>a</sup>	8.0		0.24		1.4		0.40		150	
	MST027-QA3 <sup>b</sup>	8.8	J	0.54		2.3	J	1.6	U	130	
	RD	-0.095		-0.83		-0.50		-1.5		0.14	
Angus Creek, Above Blackfoot River	MST126-QA2 <sup>a</sup>	5.3		0.67		2.8		0.86		120	
	MST126-QA3 <sup>b</sup>	5.8	J	0.63		2.0	J	1.6	U	140	
	RD	-0.090		0.062		0.34		-0.63		-0.15	
Angus Creek, Above Rasmussen Creek	MST128-QA2 <sup>a</sup>	6.3		0.21		0.11	U	0.58		83	
	MST128-QA3 <sup>b</sup>	7.1	J	0.26		1.5	J	1.6	U	88	
	RD	-0.12		-0.21		-3.4		-1.1		-0.059	
Angus Creek, below Wooley Valley Mine	MST129-QA2 <sup>a</sup>	8.4		0.44		2.9		0.48		84	
	MST129-QA3 <sup>b</sup>	8.8	J	0.54		2.3	J	1.5	U	100	
	RD	-0.047		-0.21		0.23		-1.2		-0.17	
<i>mean of RD</i>		-0.089		-0.39		-0.88		-1.0		-0.094	
<i>standard deviation of RD</i>		0.027		0.38		1.5		0.39		0.15	
<i>sample size</i>		5		5		5		5		5	
<i>mean<sub>0.025</sub></i>		-0.12		-0.86		-2.8		-1.5		-0.27	
<i>mean<sub>0.975</sub></i>		-0.056		0.090		1.0		-0.52		0.087	
<b>NOTES:</b> <sup>a</sup> ACZ QA station result. <sup>b</sup> U of I QA station result. (RD) - Relative Difference between the UI lab result and the ACZ lab results. For each sample station, the RD has been calculated. If the RD > 0.70, the result has been shaded. For each analyte, the 95% two-sided confidence bound has been calculated. If the bounds do not encompass zero, the result has been shaded. <b>Data qualifier definitions are:</b> (U) - The material was analyzed for, but was not detected above the level of the associated value. These values have been censored and are equal to one-half the reporting limit. (J) - The associated value is an estimated quantity.											